The mixed anion mineral parnauite $Cu_9[(OH)_{10}|SO_4|(AsO_4)_2]\cdot 7H_2O$ –a Raman spectroscopic study

Ray L. Frost • **and Eloise C. Keeffe**

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

Abstract

The mixed anion mineral parnauite $Cu_9[(OH)_{10}|SO_4|(AsO_4)_2]\cdot 7H_2O$ from two localities namely Cap Garonne Mine, Le Pradet, France and Majuba Hill mine, Pershing County, Nevada, USA has been studied by Raman spectroscopy. The Raman spectrum of the French sample is dominated by an intense band at 975 cm^{-1} assigned to the $\nu_1 (SO_4)^{2-}$ symmetric stretching mode and Raman bands at 1077 and 1097 cm^{-1} may be attributed to the $\nu_3 (SO_4)^{2-}$ antisymmetric stretching mode. Two Raman bands 1107 and 1126 cm^{-1} are assigned to carbonate CO_3^{2-} symmetric stretching bands and confirms the presence of carbonate in the structure of parnauite. The comparatively sharp band for the Pershing County mineral at 976 cm^{-1} is assigned to the $\nu_1 (SO_4)^{2-}$ symmetric stretching mode and a broad spectral profile centered upon 1097 cm^{-1} is attributed to the $\nu_3 (SO_4)^{2-}$ antisymmetric stretching mode. Two intense bands for the Pershing County mineral at 851 and 810 cm^{-1} are assigned to the $\nu_1 (AsO_4)^{3-}$ symmetric stretching and $\nu_3 (AsO_4)^{3-}$ antisymmetric stretching modes. Two Raman bands for the French mineral observed at 725 and 777 cm^{-1} are attributed to the $\nu_3 (AsO_4)^{3-}$ antisymmetric stretching mode. For the French mineral, a low intensity Raman band is observed at 869 cm^{-1} and is assigned to the $\nu_1 (AsO_4)^{3-}$ symmetric stretching vibration. Chemical composition of parnauite remains open and the question may be raised is parnauite a solid solution of two or more minerals such as a copper hydroxy-arsenate and a copper hydroxy sulphate.

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

Key words: parnauite, strashimirite, arsenate minerals, Raman spectroscopy, sulphate, hydroxyl, molecular water

INTRODUCTION

Parnauite $Cu_9(AsO_4)_2(SO_4)(OH)_{10}\cdot 7H_2O$ is an uncommon mixed anion mineral containing both sulphate and arsenate [1-3] . Parnauite is a secondary Cu-sulphate-arsenate. The structure of this mineral is not defined [4, 5]. The mineral is probably orthorhombic with point group 2/*m* 2/*m* 2/*m*. Sometimes the mineral is found with other minerals such as leogangite, goudeyite and strashimirite. Fibrous varieties and crusts may be confused with strashimirite. Another similar formulated mineral is leogangite $Cu_{10}(AsO_4)_4(SO_4)(OH)_6\cdot 8H_2O$. Other minerals containing sulphate and arsenate with the copper cation are arsentsumebite, arthurite, chalcophyllite, clinotyrolite, gatrellite and thometzekite. Parnauite is formed as one of supergene product of weathering of primary copper minerals (chalcopyrite, tennantite). Originally, it was found at Majuba Hill Mine, Pershing County, Nevada (U.S.A), in association with chrysocolla and other supergene minerals. Parnauite was found later also on many further localities, however, always as a very rare mineral species. No X-ray single crystal structure data are as yet available. The mineral parnauite contains four vibrational spectroscopically distinct units, namely arsenate, sulphate and hydroxyl units as well as water. The mineral is a mixed anion mineral and is one of a number of mixed anion minerals including minerals of the tsumcorite group and minerals such as peisleyite and strashimirite. Mixed anion minerals are more common than might be expected. Isomorphous substitution for arsenate by other anions such as sulphate results in the mineral parnauite. Chemical composition of parnauite has been open, because some authors assume that this mineral may contain various content of carbonate ions [6].

This research forms part of a comprehensive study of the molecular structure of secondary minerals containing oxy-anions, including uranyl minerals, formed in the oxide zone, using Raman and infrared spectroscopy. Raman spectroscopy has proven most useful for the determination of the molecular structure of minerals [7-16]. The mineral parnauite is an interesting mineral because it is a mixed anion mineral containing both sulphate and arsenate ions as well as hydroxyl ions. As such the Raman spectra will show bands typical of each of these vibrating units. The exact structure of the mineral parnauite is unknown. Raman spectroscopy is a very powerful technique for the determination of molecular structure of minerals when the exact structure from X-ray diffraction is unknown or uncertain. The objective of this research is to compare the Raman properties of parnauite

from Cap Garonne Mine, Le Pradet, France and Majuba Hill mine, Pershing County, Nevada, USA, and relate the Raman spectra to the structure of the mineral.

EXPERIMENTAL

Minerals

The parnauite minerals were supplied by The Mineralogical Research Company. The two parnauite mineral samples originated from parnauite from Cap Garonne Mine, Le Pradet, France (sample A) and Majuba Hill mine, Pershing County, Nevada, USA (sample B). The chemical composition of the mineral has been published [17]. The analysis of the parnauite from Majuba Hill, Nevada, USA, by electron microprobe corresponds to $Cu_{8.76}Al_{0.10}[(AsO_4)1.43(PO_4)_{0.43}]\_=1.86(SO_4)_{0.94}(CO_3)_{0.19}$ $(OH)_{9.98} \bullet 6.81H_2O$. The mineral analysed as $Cu_9(AsO_4)_2(SO_4)(OH)_{10}\cdot 7H_2O$. Sample A from Cap Garonne mine, France is associated with cyanotrichite, brochantite, lavendulan, mansfieldite–scorodite, chalcopyrite, cornubite. Sample B from Majuba Hill, Nevada, USA, has paragenetic relationships with the minerals spangolite, chalcophyllite, chenevixite, goudeyite, malachite, azurite brochantite and chrysocolla

Raman spectroscopy

The crystals of parnauite were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a nominal resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Details of the experimental procedure have been published. The spatial resolution of the instrument is , 1 μm. Thus if crystals are less than this value, a mixture of crystals will be measured. However the crystals of parnauite used in this experiment were > 1 1 μm. Thus any presence of for example carbonate is therefore assumed to be part of the crystal structure.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

Raman spectroscopy of the arsenate anion

In aqueous systems, the sulphate anion is of T_d symmetry and has symmetric stretching mode (ν_1) at 981 cm^{-1}, the antisymmetric stretching mode (ν_3) at 1104 cm^{-1}, the symmetric bending mode (ν_2) at 451 cm^{-1} and the ν_4 mode at 613 cm^{-1} [18, 19]. The Raman spectrum of the mineral chalcanthite shows a single symmetric stretching mode at 984.7 cm^{-1}. Two ν_2 modes are observed at 463 and 445 cm^{-1} and three ν_3 modes at 1173, 1146 and 1100 cm^{-1}. The ν_4 mode is observed as a single band at 610 cm^{-1}. The arsenate ion, $(AsO_4)^{3-}$, is a tetrahedral unit with T_d symmetry and exhibit four fundamental vibrations: the symmetric stretching vibration ν_1 (A_1) (818 cm^{-1}), the doubly degenerate bending vibration ν_2 (E) (350 cm^{-1}), the triply degenerate antisymmetric stretching vibration ν_3 (F_2) (786 cm^{-1}), and the triply degenerate bending vibration ν_4 (F_2) (398 cm^{-1}). The F_2 modes are Raman and infrared active, whereas A_1 and E modes are Raman active only. According to Frost *et al.* the ν_1 $(AsO_4)^{3-}$ vibration may coincide with the ν_3 $(AsO_4)^{3-}$ vibration. It should be noted that the wavenumber of the ν_1 $(AsO_4)^{3-}$ may be greater than that of the ν_3 $(AsO_4)^{3-}$ which is an inversion of the normal behavior shown by most tetrahedral ions, although such an inversion is not unique [20, 21]. According to Myneni *et al.* [22], the Td symmetry of $(AsO_4)^{3-}$ unit is rarely preserved in minerals and synthetic compounds, because of its strong affinity to protonate, hydrate, and complex with metal ions. Such chemical interactions reduce $(AsO_4)^{3-}$ tetrahedral symmetry to either C_{3v}/C_3 (corner sharing), C_{2v}/C_2 (edge-sharing, bidentate

binuclear), or C_1/C_s (corner sharing, edge-sharing, bidentate binuclear, multidentate]. This symmetry lowering is connected with activation of all vibrations in infrared and Raman spectra and splitting of doubly and triply degenerate vibrations. Nine normal modes may be Raman and infrared active in the case of the lowest C_s symmetry [23].

Raman spectroscopy of parnauite

The Raman spectrum of parnauite of samples A and B in the 700 to 1200 cm^{-1} region is displayed in Figs. 1 and 2. This region includes the symmetric stretching region of both the $(AsO_4)^{3-}$ units and the $(SO_4)^{2-}$ ions. The Raman spectrum of sample A in this spectral region is dominated by an intense band at 975 cm^{-1} and is assigned to the ν_1 $(SO_4)^{2-}$ symmetric stretching mode. This band is not so intense for sample B (Fig. 2) and appears significantly broader. In the Raman spectrum of A, four bands are observed at 1077, 1098, 1107 and 1126 cm^{-1}. The bands centered upon 1077 and 1097 cm^{-1} may be attributed to the ν_3 $(SO_4)^{2-}$ antisymmetric stretching mode. The two higher wavenumber bands may be assigned to carbonate CO_3^{2-} symmetric stretching bands. The presence of these bands confirms the presence of carbonate in the mineral parnauite as first suggested by Kolitsch [6]. For sample B, a Raman band is observed at 1035 cm^{-1} attributed to the ν_3 $(SO_4)^{2-}$ antisymmetric stretching mode. The broad band at 1135 cm^{-1} may be ascribed to the carbonate CO_3^{2-} antisymmetric stretching mode. In this research, the Raman spectra are taken for an aligned single crystal. The spatial resolution of the instrument is ~ 1 μm and if crystals are larger than this value as is the case of the measured samples, then a spectrum of parnauite is obtained. If the crystals are << 1 μm, then the spectrum results from the scattering of incident radiation from several crystals. Thus if an impurity such as a carbonate bearing mineral was present, then the spectrum of the sample together with that of carbonate would be determined. Several authors have found that carbonate is present in parnauite minerals [6] .

For sample B, a broad envelope of overlapping bands centered upon 851 cm^{-1} is observed. Band component analysis enables bands to be resolved with two intense bands at 851 and 810 cm^{-1}. These bands are assigned to the ν_1 $(AsO_4)^{3-}$ symmetric stretching and ν_3 $(AsO_4)^{3-}$ antisymmetric stretching modes, respectively. For sample A, a low intensity Raman band is observed at 869 cm^{-1} which is assigned to the ν_1 $(AsO_4)^{3-}$ symmetric stretching

vibration. The intensity of the $(AsO_4)^{3-}$ is such that the antisymmetric band could not be identified. Two Raman bands are observed at 725 and 777 cm^{-1} which are not observed in the Raman spectrum of B. These bands may be attributed to hydroxyl deformation modes. An alternative assignment is in terms of the ν_3 $(AsO_4)^{3-}$ antisymmetric stretching mode. The observation of multiple bands is attributed to the symmetry reduction of the $(AsO_4)^{3-}$ anion as described above.

The Raman spectra of samples A and B in the 300 to 700 cm^{-1} region are shown in Figs. 3 and 4. The Raman spectra for this spectral region may be contrasted. For sample A, the bands are well defined and component bands may be resolved. For sample B, the spectra are broad and overlap. A set of three bands is observed at 597, 610 and 622 cm^{-1} and are assigned to the triply degenerate ν_4 (SO_4^{2-}) bending modes. For the parnauite from Pershing County a set of overlapping bands is observed centered upon 614 cm^{-1}. Four bands are observed at 600, 614, 620 and 632 cm^{-1}. The differences in the band positions between samples A and B is quite remarkable. The intense bands of sample A at 451, 482 and 510 cm^{-1} are attributed to the degenerate ν_4 (SO_4^{2-}) bending modes. For sample B, a broad spectral profile is observed with component bands resolved at 463, 471 and 512 cm^{-1}. The bands in the 400 to 500 cm^{-1} region are assignable to the bending ν_2 (F_2) mode. The most intense band is observed at 482 cm^{-1} with other bands at 451 and 510 cm^{-1}. The observation of multiple bands is characteristic of reduced symmetry of the AsO_4 unit in the crystal. The Raman spectra of kankite in this region show an intense band at 492 cm^{-1} and similarly pharmacosiderite shows an intense band at 475 cm^{-1}. For clinotyrolite, an intense band is observed at 493 cm^{-1} with shoulders at 462 and 505 cm^{-1}.

The intense bands at 366 and 397 cm^{-1} in the Raman spectrum of sample A, are due to the $(AsO_4)^{3-}$ ν_2 (E) bending mode. For sample B, a broad band at 380 cm^{-1} is observed. The band at 319 cm^{-1} is attributed to $(AsO_4)^{3-}$ ν_4 (E) bending mode. The band is observed at 311 cm^{-1} for sample B. A significant number of bands is observed in the 100 to 300 cm^{-1} region for sample A (Figure 5). Raman bands are observed at 107, 120, 131, 141, 150, 158, 170, 188, 197, 244 and 263 cm^{-1}. In contrast the spectral profile is broad in the Raman spectrum of sample B. Raman bands are observed at 111, 148 (broad), 176 (broad), 225, 240, 264 and 274 cm^{-1}(Figure 6). It is considered that the bands at around 244 and 263 cm^{-1} are related to water hydrogen bonding.

The Raman spectrum of samples A and B parnauite in the 3100 to 3500 cm^{-1} region are shown in Figures 7 and 8. Three distinct Raman bands are observed for sample A at 3255, 3372 and 3410 cm^{-1} with a component band at 3402 cm^{-1}. The first band at 3255 cm^{-1} is attributed to water OH stretching bands. The two bands at 3372 and 3410 cm^{-1} are assigned to the hydroxyl stretching vibrations. Studies have shown a strong correlation between OH stretching frequencies and both the O···O bond distances and the H···O hydrogen bond distances. The elegant work of Libowitzky [43] showed that a regression function can be employed relating the above correlations with regression coefficients better than 0.96 [43]. The function is $\nu_1 = (3592 - 304) \times 109^{\frac{-d(O-O)}{0.1321}}$ cm^{-1}. Two types of OH units are identified in the structure and the known hydrogen bond distances used to predict the hydroxyl stretching frequencies. Thus if we calculate the hydrogen bond distances using the Libowitzky type formula, the 3410 cm^{-1} band provide a hydrogen bond distance of 2.805(3) Å, 3372 cm^{-1} gives 2.780(2) Å, 3255cm^{-1} gives 2.723(9) Å. The spectrum of parnauite may be divided into two groups of OH stretching wavenumbers: namely 3500–3700 cm^{-1} and 2900–3500 cm^{-1}. This distinction suggests that the strength of the hydrogen bonds as measured by the hydrogen bond distances can also be divided into two groups. An arbitrary cut-off point may be 2.74 Å based upon the wavenumber 3300 cm^{-1}. The hydrogen bond distances 2.805(3) Å may be described as weak hydrogen bonding and the bond distances of 2.780(2) and 2.723(9) Å as slightly stronger hydrogen bonds. Thus by using the position of the bands in the Raman spectrum, an estimate of the hydrogen bond distances can be made. Such values are difficult to obtain from single crystal X-ray diffraction data. Hydrogen bond distances can be obtained from neutron diffraction data but such studies are very rare.

Recently the Raman spectrum of parnauite from Slovak Republic was published (JRS in press). Three bands for the Slovak parnauite which are attributed to OH stretching vibrations are observed at 3348, 3494 and 3566 cm^{-1}. The sharp band at 3566 cm^{-1} is assigned to the OH stretching vibration of the hydroxyl units. The two bands at 3348 and 3494 cm^{-1} are assigned to water stretching modes. Hydrogen plays an extremely important role in the structure and chemistry of oxysalt minerals such as for mixed arsenate sulphates including parnauite and peisleyite [24]. The presence of water adds to the stability of the oxysalt. [25] For any crystal structure the structural unit may be defined as the strongly bonded part of the unit. Structural units are linked together by interstitial species such as

univalent and divalent cations and by water groups that are involved in much weaker bonding.

CONCLUSIONS

Raman spectroscopy has been used to characterise the molecular structure of the mineral parnauite $Cu_9(AsO_4)_2(SO_4)(OH)_{10}\cdot 7H_2O$. Characteristic Raman bands of the $(AsO_4)^{3-}$ stretching and bending vibrations were identified and described. Raman bands attributable to the OH stretching vibrations of water and hydroxyl units were analysed.

Considerable differences in the Raman spectra of the two parnauite minerals from the two localities Cap Garonne Mine, Le Pradet, France and Majuba Hill mine, Pershing County, Nevada, USA are observed and reported. The crystal structure of parnauite remains unsolved. Raman spectroscopy proves the presence of carbonate anion in the mineral structure. The question of the exact nature of the mineral parnauite remains somewhat unanswered. Chemical composition of parnauite remains open, because some authors assume that this mineral may contain various content of carbonate ions [6].

Acknowledgments

The financial and infra-structure support of the Queensland University of Technology, Inorganic Materials Research Program is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

REFERENCES

[1] L. Lai, Y. Li, N. Shi, Yanshi Kuangwuxue Zazhi 16 (1997) 50-55.

[2] H. Sarp, J. Deferne, B.W. Liebich, Arch. Sc. 31 (1978) 213-217.

[3] W.S. Wise, Amer. Min. 63 (1978) 704-708.

[4] H. Sarp, J. Deferne, B.W. Liebich, 31 (1978) 213-217.

[5] W.S. Wise, 63 (1978) 704-708.

[6] U. Kolitsch, Aufschluss 48 (1997) 65-91.

[7] S. Bahfenne, R.L. Frost, Spectrochim. Acta, A74 (2009) 100-103.

[8] S. Bahfenne, R.L. Frost, Spectrochim. Acta, A74 (2009) 625-628.

[9] R.L. Frost, Spectrochim. Acta, A71 (2009) 1788-1794.

[10] R.L. Frost, Spectrochim. Acta, A72 (2009) 903-906.

[11] R.L. Frost, S. Bahfenne, J. Graham, Spectrochim. Acta, A71 (2009) 1610-1616.

[12] R.L. Frost, J. Cejka, Spectrochim. Acta, A 71 (2009) 1959-1963.

[13] R.L. Frost, J. Cejka, M.J. Dickfos, Spectrochim. Acta, A71 (2009) 1799-1803.

[14] R.L. Frost, M.J. Dickfos, Spectrochim. Acta, A72 (2009) 445-448.

[15] R.L. Frost, M.J. Dickfos, E.C. Keeffe, Spectrochim. Acta, A71 (2009) 1663-1666.

[16] R.L. Frost, M.J. Dickfos, E.C. Keeffe, Spectrochim. Acta, A71 (2009) 1512-1515.

[17] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Handbook of Mineralogy IV, Arsenates, phosphates, vanadates., Mineral Data Publishing, Tucson, Arizona 2000.

[18] R.L. Frost, J.T. Kloprogge, Neues Jahrb. Mineral., Monatsh. (2001) 27-40.

[19] W. Martens, R.L. Frost, J.T. Kloprogge, P.A. Williams, J. Raman Spectros. 34 (2003) 145-151.

[20] F.K. Vansant, B.J.V.d. Veken, H.O. Desseyn, J. Mol. Struct. 15 (1973) 425-437.

[21] R.H. Busey, O.L. Keller, J. Chem. Phys. 41 (1964) 215-225.

[22] S.C.B. Myneni, S.J. Traina, G.A. Waychunas, T.J. Logan, Geochim. Cosmochim. Acta 62 (1998) 3285-3300.

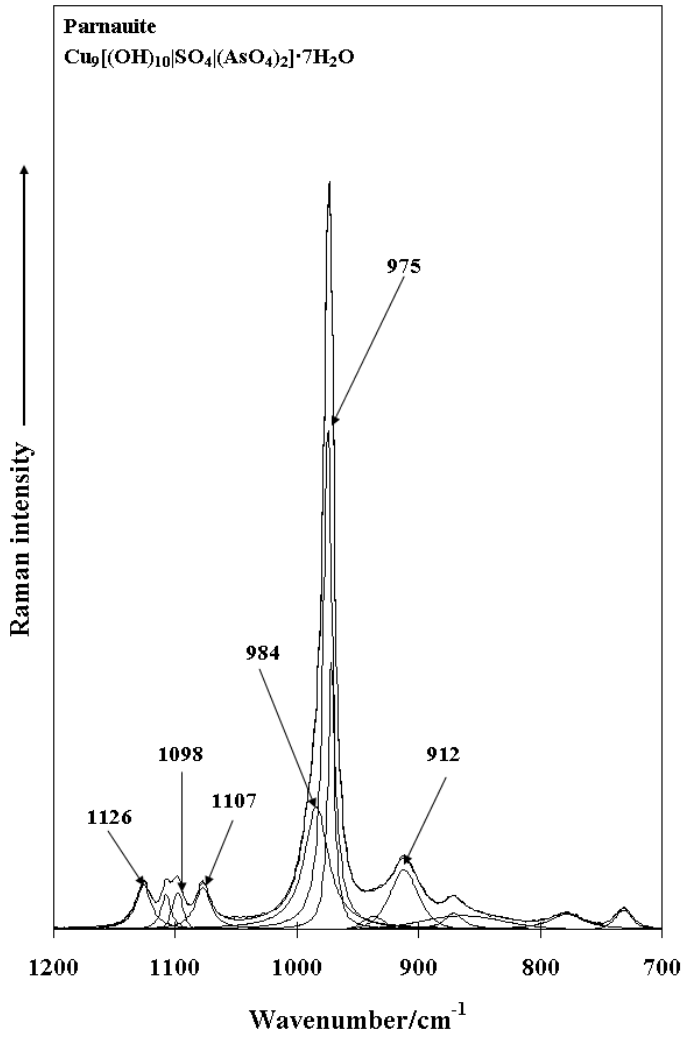
[23] S.D. Ross, in: V.C. Farmer (Ed.), The infared spectra of minerals Mineralogical Society, London 1974.

[24] D.M.C. Huminicki, F.C. Hawthorne, Rev. Min. Geochem. 48 (2002) 123-325.

[25] F.C. Hawthorne, Zeit. Krist. 201 (1992) 183-206.

List of Figures

306



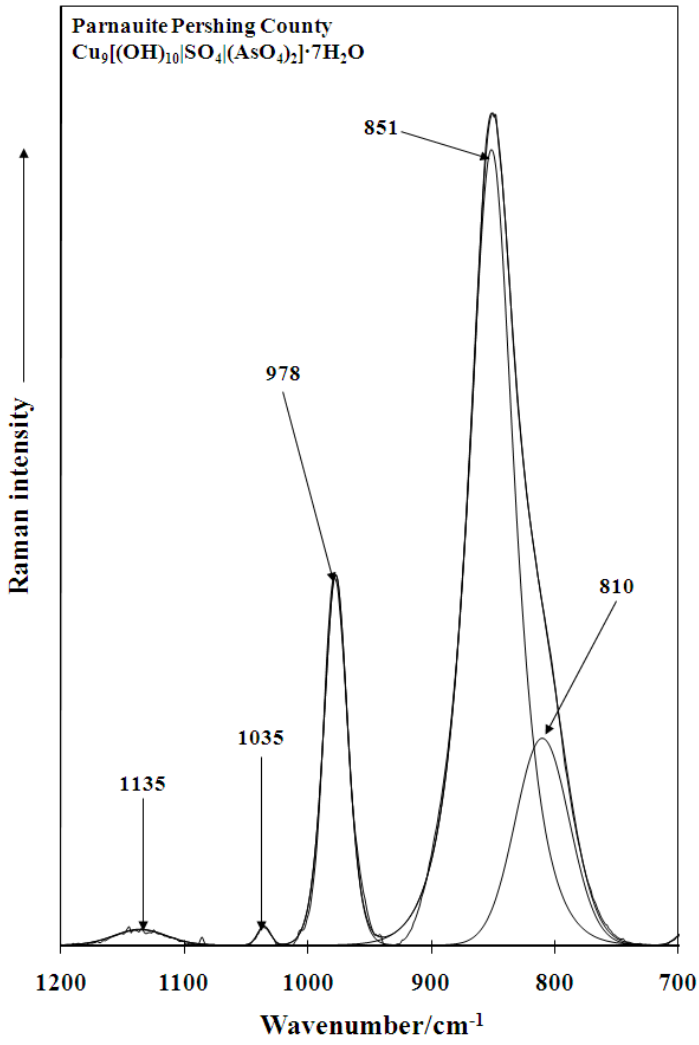
307

308

309 **Figure 1**

310

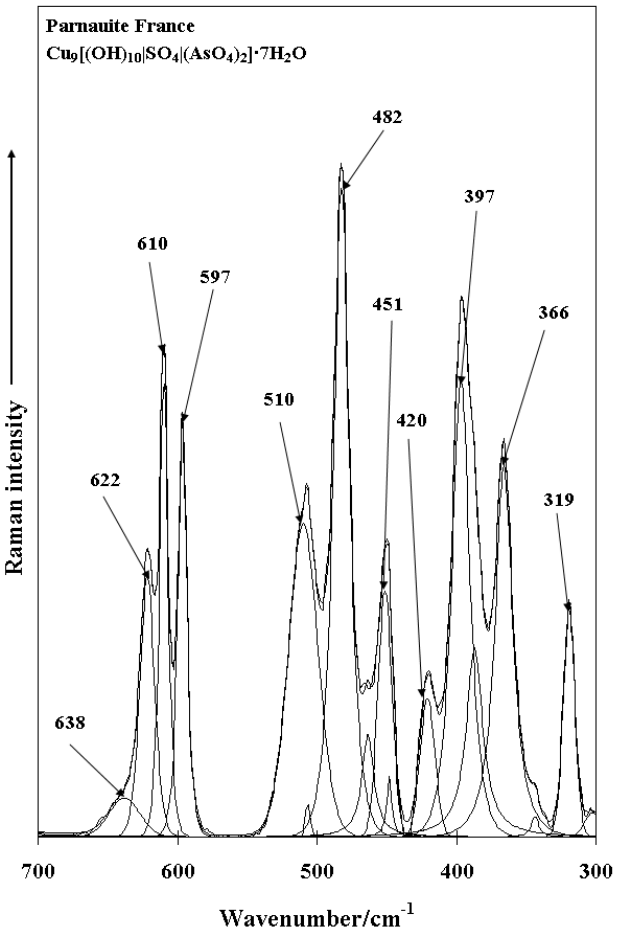
311



312

313

314 **Figure 2**



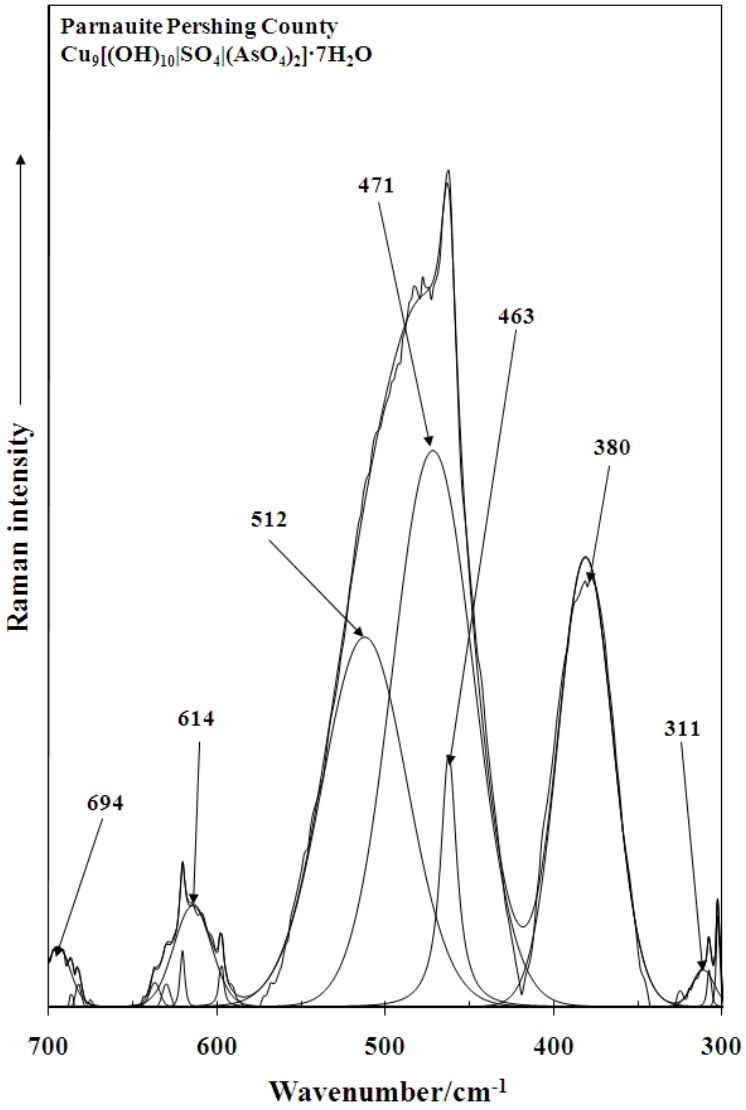
315

316

317 **Figure 3**

318

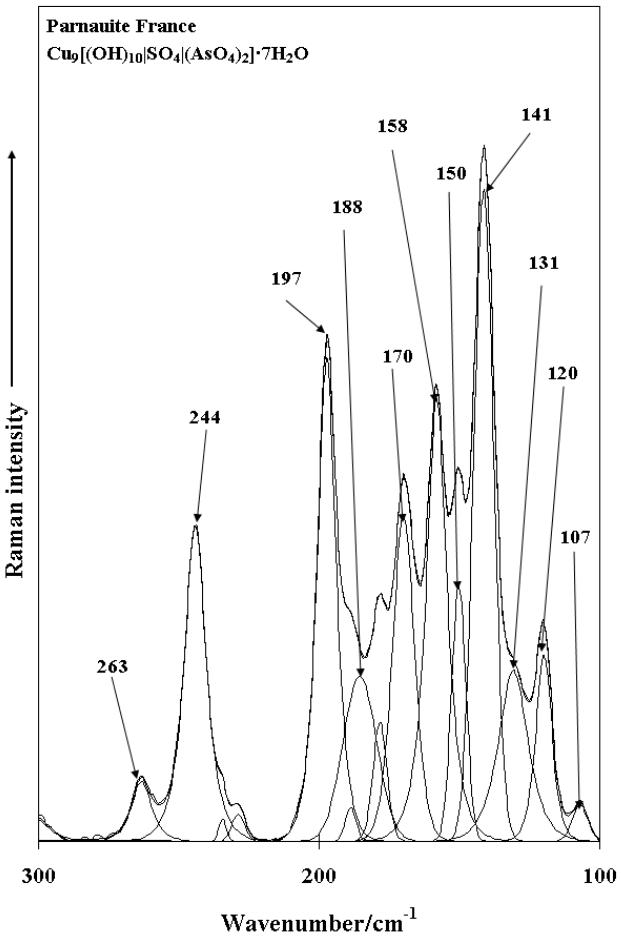
319



320

321

322 **Figure 4**



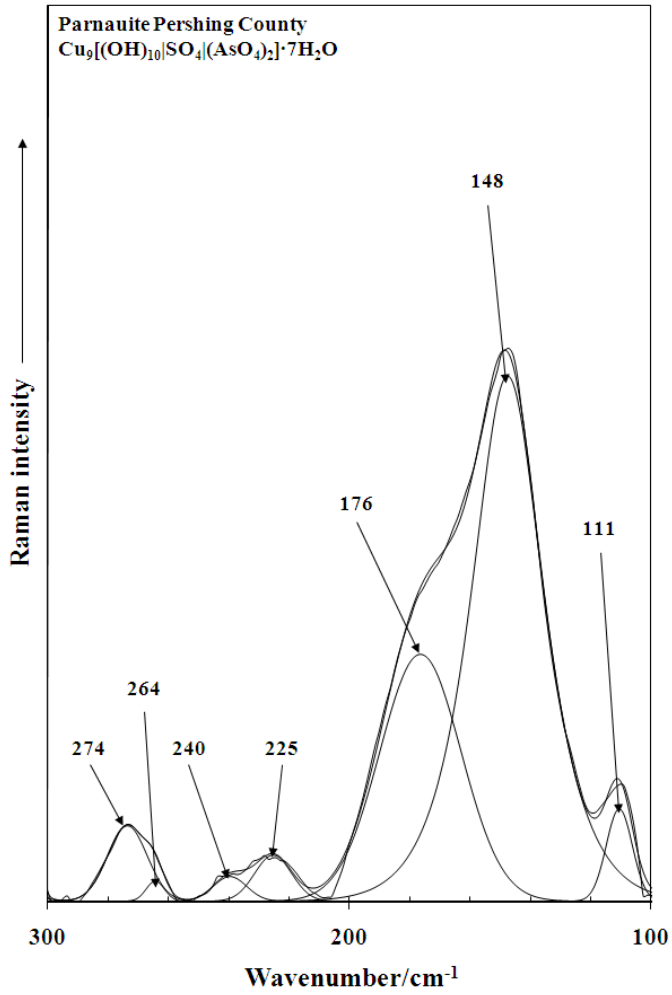
323

324

325 **Figure 5**

326

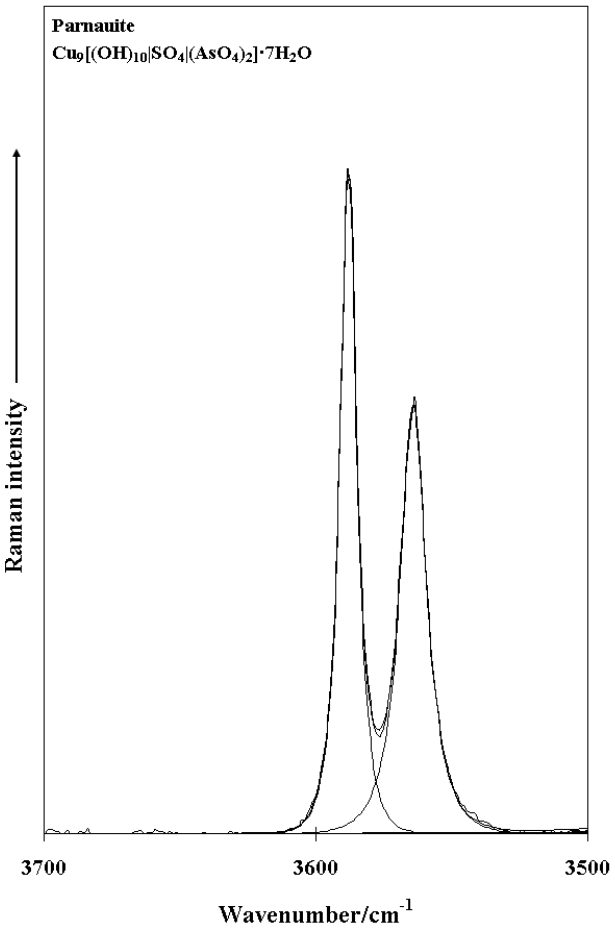
327



328

329

330 **Figure 6**



331

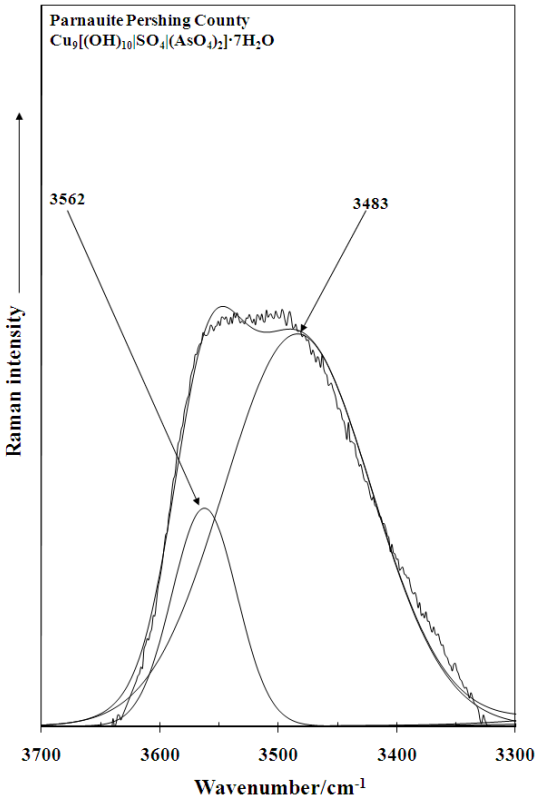
332

333 **Figure 7**

334

335

336



337

338

339 **Figure 8**

340

341